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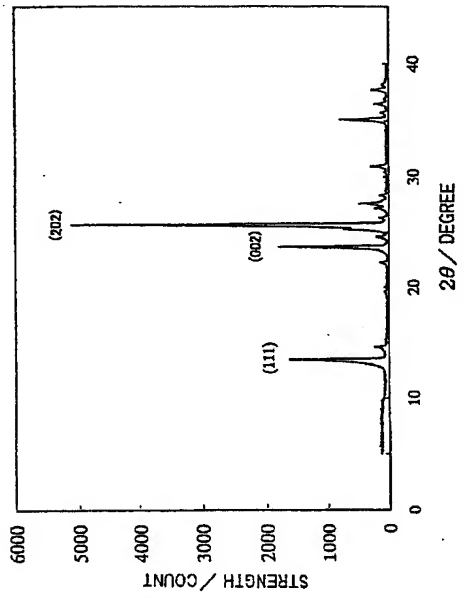
(54) Mordenite zeolite membrane and method for producing the same

(57) A mordenite (MOR) zeolite membrane is formed on a porous substrate and dominantly oriented in a specific crystalline direction. A method for producing a mordenite (MOR) zeolite membrane includes the steps of: immersing a porous substrate in a gel of raw material which contains zeolite constitution elements and contains 40-400 of SiO_2/Al_2O_3 in molar ratio, 10-120 of H_2O/Na_2O in molar ratio, and 10 40 of H_2O/SiO_2 in molar ratio, and subjecting the gel in the presence of the porous substrate to hydrothermal synthesis at 150°C or more to make zeolite crystallized to form a membrane thereof. The MOR zeolite membrane is oriented in a specific crystalline direction.

FIG.4



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Description

Background of the Invention and Related Art Statement

[0001] The present invention is directed to an MOR zeolite membrane which is dominantly oriented in a specific crystalline direction and a method for producing the membrane. Zeolite has a frame structure of crystalline aluminosilicate and a mesh-like structure composed of fine pores of a minute uniform diameter. Thus, zeolite is used as a molecule sieve or a catalyst.

[0002] For example, JP-A-7-330326 discloses a zeolite membrane which is formed on a single crystal substrate of an oxide, a semiconductor or a metal and oriented in a specific crystalline direction, and zeolite membranes of A type, Y type and the like are given in the examples.

[0003] In addition, WO92/13631 discloses zeolite membranes comprising an oriented single layer of ZSM-5 (MFI), an A type, a Y type, an X type and the like. WO97/25272 discloses an MFI zeolite membrane oriented along the b axis and a method for producing the membrane. Further, WO96/01683 discloses an MFI zeolite membrane oriented along the a axis and the c axis and the method for producing the membrane.

[0004] However, a mordenite (MOR) zeolite membrane oriented in a specific crystalline direction is not known till now. An MOR zeolite membrane is superior in acid resistance in comparison with zeolite membranes of an A type, a Y type and the like, and it is extremely useful if such an MOR zeolite membrane can be obtained.

Summary of the Invention

[0005] The present invention aims to provide an MOR zeolite membrane dominantly oriented in a specific crystallization direction and a method for producing the membrane. According to the present invention, there is provided a mordenite (MOR) zeolite membrane formed on a porous substrate and dominantly oriented in a specific crystalline direction.

[0006] According to the present invention, there is further provided a method for producing a mordenite (MOR) zeolite membrane comprising the steps of:

> immersing a porous substrate in a gel of raw material which contains zeolite constitution elements and contains 40-400 of SiO_2/Al_2O_3 in molar ratio, 10-120 of H_2O/Na_2O in a molar ratio, and 10-40 of H_2O/SiO_2 in molar ratio, and
> subjecting the gel in the presence of the porous substrate to hydrothermal synthesis at 150°C or more to make zeolite crystallized to form a membrane thereof.

[0007] In the above, it is preferable that the porous substrate is disposed in a reaction vessel so that a surface on which a membrane is formed becomes perpendicular, and that the gel of the raw material contains SiO_2/Al_2O_3 of 100-400 in molar ratio, H_2O/Na_2O of 10-100 in molar ratio, and H_2O/SiO_2 of 10-30 in molar ratio.

Brief Description of the Drawings

[0008]

> Fig. 1(a) is an SEM photograph showing a crystal structure of a surface of the membrane obtained in Example 1, and Fig. 1(b) is an SEM photograph showing a crystal structure of a section of the membrane obtained in Example 1.
> Fig. 2(a) is an SEM photograph showing a crystal structure of a surface of the membrane, and Fig. 2 (b) is an SEM photograph showing a crystal structure of a section of the membrane obtained in Example 2.
> Fig. 3 is an SEM photograph showing a crystal structure of a section of the membrane obtained in Example 3.
> Fig. 4 is a graph showing an X-ray diffraction pattern of the membrane obtained in Example 3.
> Fig. 5 is an SEM photograph showing a crystal structure of a section of the membrane obtained in example 4.

Detailed Description of the Invention

[0009] The present invention is hereinbelow described in detail.

[0010] The present invention is a mordenite (MOR) zeolite membrane dominantly oriented in a specific crystalline direction and formed on a porous substrate.

[0011] Such an MOR zeolite membrane can be produced by immersing a porous substrate in a gel of raw material containing zeolite constitution elements having a specific composition and subjecting the gel in the presence of the porous substrate to hydrothermal synthesis at 150°C or more.

[0012] In the above MOR zeolite membrane, the crystalline direction is not particularly limited and, it is oriented along any one of the **a** axis, **b** axis and **c** axis. This MOR zeolite membrane has a high ratio of silica and is superior in acid resistance in comparison with an A-type zeolite membrane and a Y-type zeolite membrane, and therefore can be applied for use requiring acid resistance in fields of molecule sieves and catalysts.

[0013] Next, a method for producing the above MOR zeolite membrane is described.

[0014] As a raw material, there is used a raw material sol constituted by a simple substance including silicon, aluminum, and an alkali metal, which are zeolite constitution elements, a compound thereof, and the like.

[0015] It is important that the gel of raw material has a composition range of 40-400 of SiO_2/Al_2O_3 in molar

ratio, 10-120 of H_2O/Na_2O in molar ratio, and 10-40 of H_2O/SiO_2 in molar ratio. In the case that a raw material has a composition outside the about range, an MOR zeolite membrane dominantly oriented in a specific crystalline direction may not be obtained. As a composition range of the raw materials, it is more preferable that the molar ratio of SiO_2/Al_2O_3 is 100-400, the molar ratio of H_2O/Na_2O is 10-100, and the molar ratio of H_2O/SiO_2 is 10-30.

[0016] Next, a porous substrate is immersed in the raw-material gel having the above composition range. In the present invention, not a generally-used dense substrate but a porous substrate is employed. A material for a porous substrate is not limited, and various kinds of materials such as ceramics, metals and the like may be used. There is exemplified, as a non-limited example, a substrate made of a ceramic of general oxide such as alumina, zirconia, titania, silica, or the like; a compound oxide such as silicazirconia, silicatitania, or the like; and a substrate made of a metal such as iron, stainless steel, copper, tantalum, or the like.

[0017] Membrane formation by crystallization is performed by subjecting a gel of raw material for zeolite to hydrothermal synthesis with putting a porous substrate having a seed crystal applied thereon in an autoclave. The important thing here is to perform hydrothermal synthesis at a temperature of 150°C or more. If a temperature of hydrothermal synthesis is below 150 °C, an MOR zeolite membrane dominantly oriented in a specific crystalline direction may not be produced. It is required that a temperature of hydrothermal synthesis is 150°C or more for securing an orientation property. It is more preferable that the hydrothermal synthesis is at 165 - 195°C, e.g. e.g. 165 - 175°C, and it is particularly preferable that the temperature is around 180°C.

[0018] In addition, it is preferable in the present inventive process to dispose a porous substrate in a reaction vessel so that a surface of said substrate on which a membrane is formed becomes perpendicular. The expression "dispose the substrate perpendicularly" means that the substrate is disposed in a reaction vessel in such a manner that the substrate surface on which membrane is formed is placed perpendicularly to the ground. Thus, by performing hydrothermal synthesis with a porous substrate being disposed perpendicularly in a reaction vessel, a crystallized MOR zeolite membrane dominantly oriented along the b axis or the c axis may be produced. In the case that a porous substrate is disposed in a reaction vessel so that a surface of the substrate on which a membrane is formed becomes horizontal to the ground, one may obtain an MOR zeolite membrane having only a lower layer being oriented in a specific crystalline direction, with a not-oriented upper layer.

[0019] Incidentally, a so-called seeding step, in which a seed crystal is applied beforehand upon crystallizing by using hydrothermal synthesis is not required in producing an MOR zeolite membrane of the present invention. However, it is preferable to perform a seeding step because a dense zeolite membrane may be obtained, and as a consequence a membrane having a good separation performance may be obtained.

[0020] The present invention is hereinbelow described with reference to Examples and Comparative Examples in more detail. However, the present invention is not limited thereto.

(Example 1: b-axis oriented MOR zeolite membrane)

[0021] 0.425g of sodium aluminate was mixed with sodium hydroxide solution (7.26gNaOH+28.8gH_2O) to give a mixture, and the mixture was sufficiently stirred at room temperature (20°C). 72g of colloidal silica (30wt% SiO_2 + 0.6wt% Na_2O) was added to the resultant, and it was sufficiently mixed at 50°C till a transparent solution was obtained. The resultant raw material gel had a molar ratio of $10Na_2O : 0.15Al_2O_3 : 36SiO_2 : 440H_2O$.

[0022] The surface of a porous alumina tube (10mm of outer diameter, 60mm long) having a fine pore diameter of 0.1 μm was washed, and a commercial mordenite seed crystal (molar ratio: $SiO_2/Al_2O_3 = 10.2$) was applied on the surface of the substrate by a dip method. Then, they were dried by 100°C for 15 minutes. The prepared raw material gel solution was put in an autoclave, and the porous alumina tube was perpendicularly sunk in the gel by the use of a Teflon support stand. Then, the autoclave was closed. Subsequently, hydrothermal synthesis was performed at 180°C for 5 hours. After being cooled, the porous alumina tube was taken out, and a membrane formed on the surface thereof was sufficiently washed with distilled water. Then, the resultant product was dried at 100°C.

[0023] The membrane formed on the substrate was subjected to X-ray diffraction and SEM observation of a section and a surface, and it was confirmed that the membrane was a mordenite (MOR) zeolite membrane dominantly oriented along the b axis. Fig. 1(a) is an SEM photograph showing a crystal structure of a surface of the membrane, and Fig. 1(b) is an SEM photograph showing a crystal structure of a section of the membrane.

(Comparative Example 1)

[0024] The same procedure as in Example 1 was repeated until the hydrothermal synthesis, which was performed at 100°C for 2 weeks. After being cooled, the porous alumina tube was taken out, and a membrane formed on the surface of the substrate was sufficiently washed with distilled water. Then, the resultant product was dried at 100°C.

[0025] The membrane formed on the substrate was subjected to X-ray diffraction and SEM observation of a section and a surface, in which no X-rays diffraction peak was recognized, and the membrane was con-

firmed to be amorphous.

(Example 2: c-axis oriented MOR zeolite membrane)

[0026] 3.7045g of aluminum sulfuric anhydride was sufficiently mixed with sodium hydroxide solution (12.595g NaOH + 40g H_2O) at room temperature to obtain a solution. A mixture of 80g of colloidal silica and 192g of water was sufficiently mixed with the above-obtained solution for 1 hour. The formed raw material gel had a molar ratio of $0.38Na_2O : 0.025Al_2O_3 : SiO_2 : 40H_2O$.

[0027] The surface of a porous alumina tube (10mm of outer diameter, 60mm long) having a fine pore diameter of 0.1 μm was washed, and a commercial mordenite seed crystal (molar ratio: $SiO_2/Al_2O_3 = 10.2$) was applied on the surface by a slurry coat method. Then, the tube was dried at 100°C for 15 minutes. The above gel was put in an autoclave, and the porous alumina tube was sunk in the gel by the use of a Teflon support stand. The autoclave was closed, and hydrothermal synthesis was performed at 180°C for 5 hours. After being cooled, the porous alumina tube was taken out, and a membrane formed on the surface was sufficiently washed with distilled water. Then, the resultant product was dried by 100°C.

[0028] The membrane formed on the substrate tube was subjected to X-ray diffraction and SEM observation of a section and a surface, and it was confirmed that the membrane was a mordenite (MOR) zeolite membrane dominantly oriented along the c axis which was oriented in parallel with a substrate of the porous alumina tube. Fig. 2(a) is an SEM photograph showing a crystal structure of a surface of the membrane, and Fig. 2(b) is an SEM photograph showing a crystal structure of a section of the membrane.

(Comparative Example 2)

[0029] 2.277g of aluminum sulfuric anhydrite was sufficiently mixed with sodium hydroxide solution (0.23g NaOH + 6g H_2O) at room temperature to a solution. 20g of colloidal silica was sufficiently mixed with the solution for 2 hours. The formed raw material gel had a molar ratio of $3Na_2O : Al_2O_3 : 20Si_2O : 200H_2O$.

[0030] The surface of a porous alumina tube (a diameter of 10mm, 60mm long) having a fine pore diameter of 0.1 μm was washed, and a commercial mordenite seed crystal (molar ratio : $SiO_2/Al_2O_3 = 10.2$) was applied on the surface by a slurry coat method. Then, the tube was dried at 100°C for 15 minutes. The above gel solution was put in an autoclave, and the porous alumina tube was sunk perpendicularly by the use of a Teflon support stand. The autoclave was closed, and hydrothermal synthesis was performed at 180°C for 5 hours. After being cooled, the porous alumina tube was taken out, and a membrane formed on the surface was sufficiently washed with distilled water. Then, the resultant product was dried at 100°C.

[0031] The membrane formed on the substrate was subjected to X-ray diffraction and SEM observation of a section and a surface, in which no X-ray diffraction peak was recognized, and the membrane was confirmed to be amorphous.

(Comparative Example 3)

[0032] 1.129g of aluminum sulfuric anhydride were sufficiently mixed with sodium hydroxide solution (3.84g NaOH + 78g H_2O) at room temperature to obtain a solution. 20g of colloidal silica was sufficiently mixed with the resultant solution for 1 hour. The formed raw materials gel had a molar ratio of $0.48Na_2O : 0.033Al_2O_3 : SiO_2 : 50H_2O$.

[0033] The surface of a porous alumina tube (10mm of outer diameter, 60mm long) having a fine pore diameter of 0.1 μm was washed, and a commercial mordenite seed crystal (molar ratio: $SiO_2/Al_2O_3 = 10.2$) was applied on the surface by a slurry coat method. Then, the tube was dried at 100°C for 15 minutes. The above gel solution was put in an autoclave, and a porous alumina tube was sunk perpendicularly in the gel by the use of a Teflon support stand. The autoclave was closed, and hydrothermal synthesis was performed at 180°C for 5 hours. After being cooled, the porous alumina tube was taken out, and a membrane formed on the surface was sufficiently washed with distilled water. Then, the resultant product was dried at 100°C.

[0034] The membrane formed on the substrate was subjected to X-ray diffraction and SEM observation of a section and a surface, in which no X ray diffraction peak was recognized, and the membrane was confirmed to be amorphous.

(Example 3: c-axis oriented MOR zeolite membrane)

[0035] A raw material was prepared and hydrothermal synthesis was performed in the same manner as in Example 2 except that a raw-material gel had a molar ratio of $0.28Na_2O : 0.0042Al_2O_3 : SiO_2 : 12.2H_2O$ and that a hydrothermal synthesis was performed at 180°C for 2 days.

[0036] The membrane formed on the substrate was subjected to X-ray diffraction and SEM observation of a section and a surface, and it was confirmed that the membrane was a mordenite (MOR) zeolite membrane dominantly oriented along the c axis which was oriented in parallel with a substrate of the porous alumina tube. Fig. 3 is an SEM photograph showing a crystal structure of a section of the membrane, and Fig. 4 is a graph showing an X-ray diffraction pattern.

(Comparative Example 4)

[0037] A raw material was prepared and hydrothermal synthesis was performed in the same manner as in Ex-

ample 3 except that hydrothermal synthesis was performed at 100°C.

[0038] The membrane formed on the substrate was subjected to X-ray diffraction and SEM observation of a section and a surface, and it was confirmed that the membrane was not oriented in a specific direction and had random orientation though crystallization was recognized.

(Comparative Example 5)

[0039] A raw material was prepared and hydrothermal synthesis was performed in the same manner as in Example 3 except that hydrothermal synthesis was performed at 140°C.

[0040] The membrane formed on the substrate was subjected to X-ray diffraction and SEM observation of a section and a surface, and it was confirmed that the membrane was not oriented in a specific direction and had random orientation though crystallization was recognized.

(Comparative Example 6)

[0041] A raw material was prepared and hydrothermal synthesis was performed in the same manner as in Example 2 except that a raw material gel had a molar ratio of $0.15Na_2O : 0.05Al_2O_3 : SiO_2 : 10H_2O$. After being cooled, the porous alumina tube was taken out, and it was found to find out that no membrane was formed on the porous alumina tube.

(Example 4)

[0042] A raw material was prepared and hydrothermal synthesis was performed in the same manner as in Example 3 except that porous alumina tube was sunk horizontally in an autoclave and that hydrothermal synthesis was performed at 180°C for 24 hours.

[0043] The membrane formed on the substrate was subjected to X-ray diffraction and SEM observation of a section and a surface, and it was confirmed that a membrane was not oriented in a layer on the upper side and dominantly oriented along c axis only in a layer on the lower side which was near the porous alumina tube substrate side though crystallization was recognized. Fig. 5 is an SEM photograph showing a crystal structure of a section of the membrane.

[0044] As discussed above, according to the present invention, there can be provided an MOR zeolite membrane oriented in a specific crystalline direction and a preferable method for producing the membrane.

Claims

1. A mordenite (MOR) zeolite membrane formed on a porous substrate and dominantly oriented in a specific crystalline direction.

2. A method for producing a mordenite (MOR) zeolite membrane comprising the steps of:

   immersing a porous substrate in a gel of raw material which contains zeolite constitution elements and contains 40-400 of SiO_2/Al_2O_3 in molar ratio, 10-120 of H_2O/Na_2O in a molar ratio, and 10-40 of H_2O/SiO_2 in a molar ratio, and subjecting the gel in the presence of the porous substrate to hydrothermal synthesis at 150°C or more to make zeolite crystallized to form a membrane thereof.

3. A method as defined in claim 2, wherein the porous substrate is disposed in a reaction vessel so that a surface of the substrate on which a membrane is formed becomes perpendicular to the reaction vessel.

4. A method as defined in claim 2 or 3, wherein as a composition range of the raw materials, the molar ratio of SiO_2/Al_2O_3 is 100-400, the molar ratio of H_2O/Na_2O is 10-100, and the molar ratio of H_2O/SiO_2 is 10-30.

FIG.1(a)

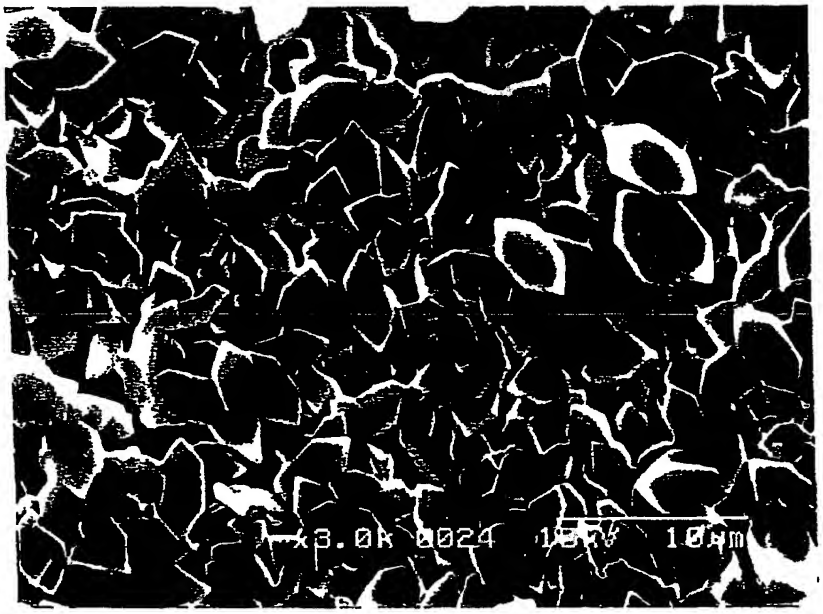


FIG.1(b)

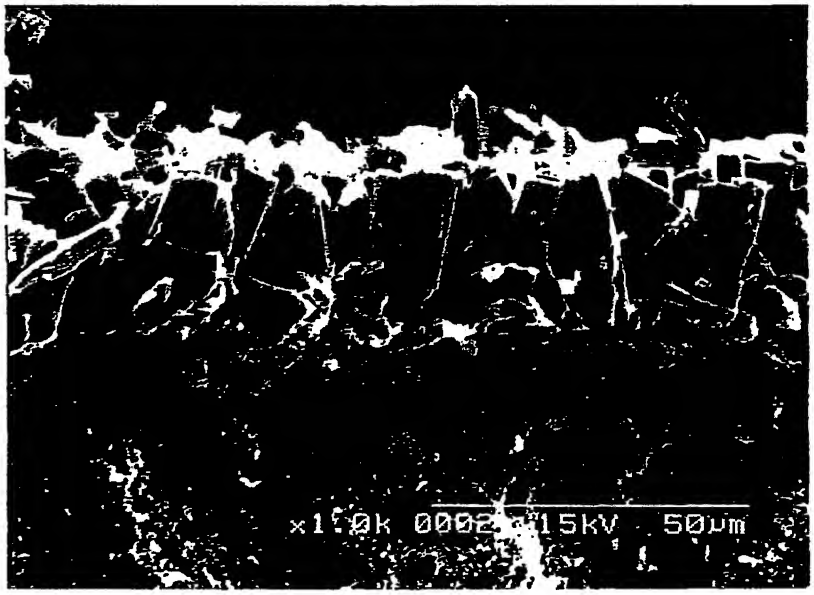


FIG.2(a)

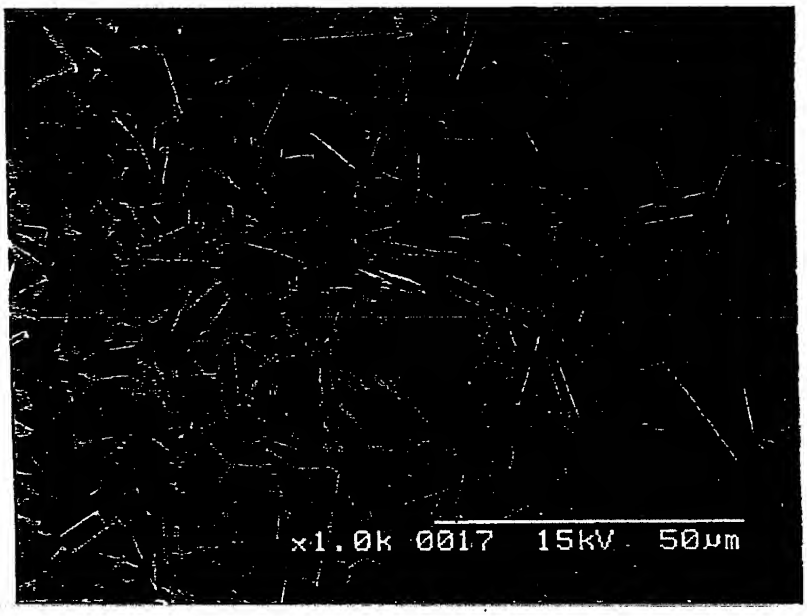


FIG.2(b)

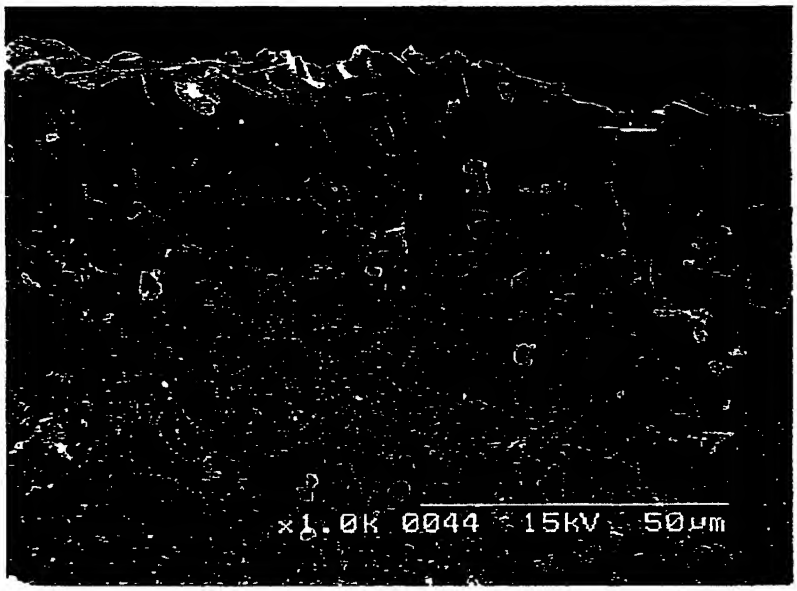


FIG.3

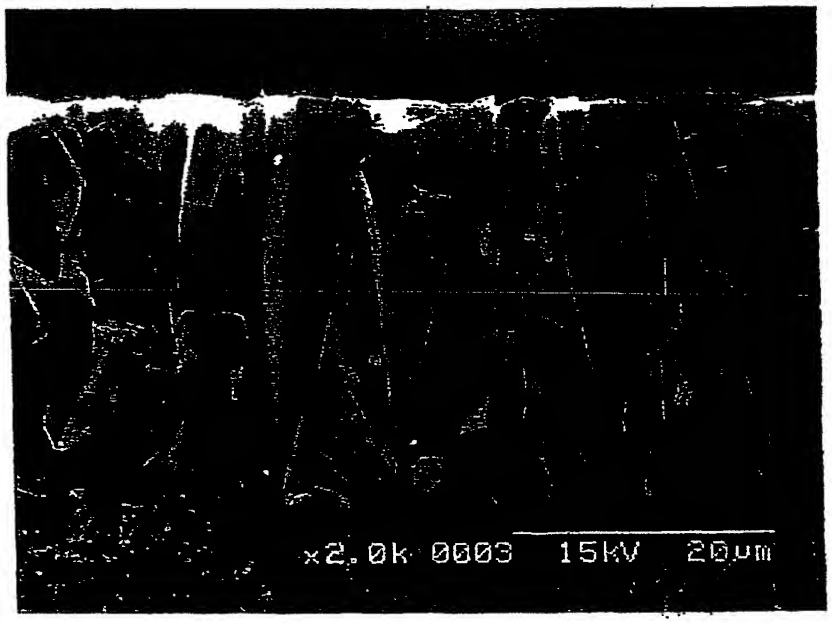
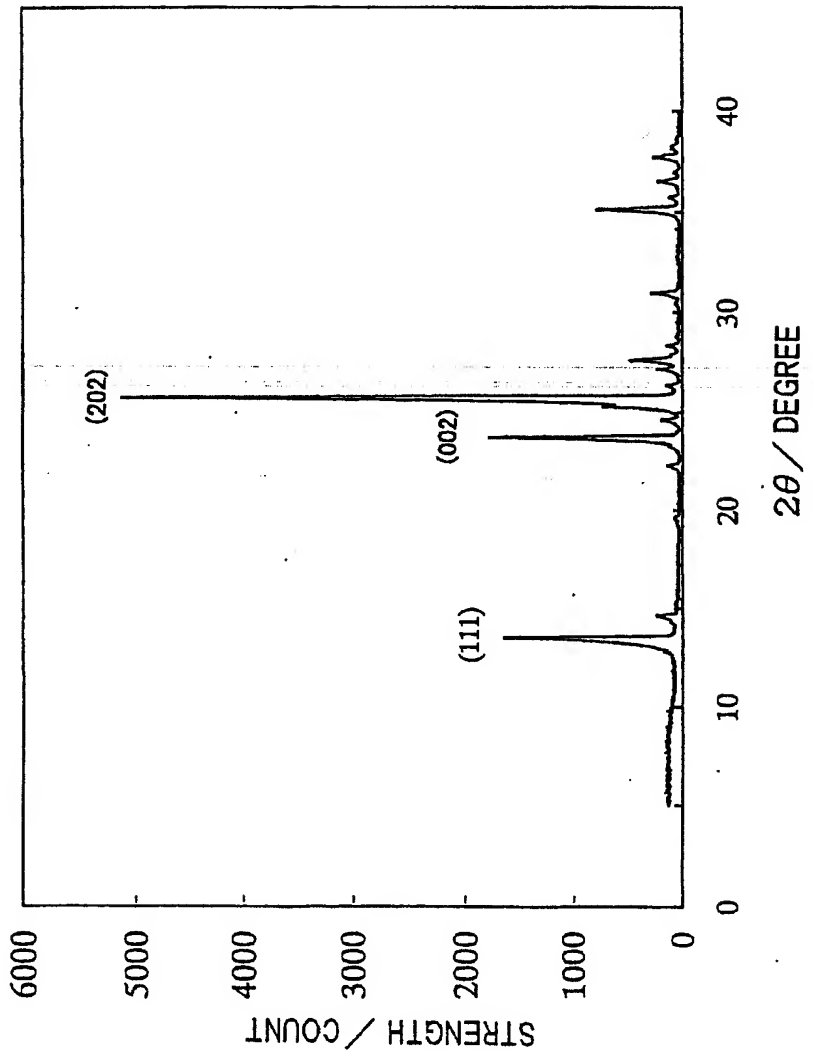


FIG.4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(002)
(111)
STRENGTH / COUNT
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5000
4000
3000
2000
1000
0
0
10
20
30
40
2θ / DEGREE

FIG.5